SUPPORTING MATERIAL

for

The Nature of the Intramolecular Charge Transfer (ICT) State in Peridinin

Nicole L. Wagner[‡], *Jordan A. Greco*[†], *Miriam M. Enriquez*[†],
Harry A. Frank[†,*] *and Robert R. Birge*[‡,†,*]

[‡]Department of Molecular & Cell Biology, University of Connecticut, Storrs, Connecticut 06269-3125 USA

[†]Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060 USA

[*]To whom correspondence should be addressed. Email: rbirge@uconn.edu or harry.frank@uconn.edu; Telephone: 860-486-6721 (RRB) or 860-486-2844 (HAF); Fax: 860-486-2981

Overview of Supporting Material

This supporting material presents additional figures and tables that are relevant to the main paper. Transient absorption spectra for longer time delays than examined in Fig. 5 of the main paper are shown in Fig. S1. The calculated ground and relaxed excited singlet state geometries of the model chromophore in *n*-hexane and methanol are shown in Fig. S2. The calculated ground and relaxed excited singlet state geometries of the full peridinin chromophore in methanol are shown in Fig. S3. EOM-CCSD calculations for the full peridinin chromophore geometries shown in Fig. S3 are provided in Fig. S4. This figure can be compared to the model chromophore calculations shown in Fig. 6 of the main paper. Analysis of the dipole moment of the full peridinin chromophore in various solvents is presented in Fig. S5.

The cartesian coordinates and Mulliken atomic charges associated with the ground state and the excited state of the model compound in methanol are presented in Tables S1 and S2. The cartesian coordinates and Mulliken atomic charges associated with the ground state and the relaxed excited singlet state of the full peridinin compound in methanol are presented in Tables S3 and S4. The ground state coordinates were generated theoretically by using B3LYP/6-31G(d) methods coupled with solvation methods based on the polarizable continuum model (PCM). The excited state coordinates were generated theoretically by using single-configuration interaction (CIS) methods and a double-zeta D95 basis set. The active space included the highest energy 8 filled molecular orbitals and the lowest energy 8 unfilled molecular orbitals. Additional details may be found in the theoretical section of the main paper.

Ground and Excited State Dipole Moments. We calculated the ground state dipole moment of both the model chromophore and the full peridinin chromophore in a variety of solvents by using density functional theory [B3LYP/6-31G(d)] and self-consistent reaction field theory based on PCM methods (see Theoretical Methods). The results for the full chromophore are plotted in Fig. S5, and two linear regions are observed when the total dipole moment is plotted versus the Onsager dielectric function,

$$P(\varepsilon) = 2(\varepsilon - 1)/(2\varepsilon + 1) \tag{1}$$

where ε is the dielectric constant, and $P(\varepsilon)$ varies from 0 ($\varepsilon = 1$, vacuum conditions) to 1 ($\varepsilon = \infty$). At relatively low dielectric constants ($\varepsilon \leq 4$), a linear fit to the data yields,

$$\mu_{\varepsilon<=4} = 5.96 + 2.77P(\varepsilon) \tag{2}$$

At dielectric constants above 4, and for polar or very polar molecules, the following relationship holds,

$$\mu_{\varepsilon>4} = 5.29 + 3.85P(\varepsilon) \tag{3}$$

As shown in Fig. S5, the linear portions are separated by a kink in the trend line at roughly $P(\varepsilon) \sim 0.6$ ($\varepsilon \sim 4$). However, examination of the solvent optimized geometries revealed nothing unusual associated with the transition between regions. It is interesting to note, however, that this is the approximate region at which meaningful populations of the ICT state are observed in the transient absorption spectra (see Fig. 5 noting that modest ICT state formation is observed in methyl-*t*-butyl ether, $\varepsilon \sim 2.6$). No experimental measurements of the ground state dipole moment have been reported, but Stark effect studies are consistent with a ground state vacuum value (μ_0) of ~6 D (*1*).

Stark measurements on peridinin (*2*) and modified length analogs of peridinin (*1*) revealed a large increase in the dipole moment of the strongly allowed "$1^1B_u^+$" state relative to the ground state value. However, the two studies did not agree on the magnitude of the dipole moment change. Premvardhan *et al.*(*2*) observed ambient temperature solvent dependent values of $\Delta\mu("^1B_u^+")$ of 22 D in methyl tetrahydrofuran and ~27 D in ethylene glycol. Kusumoto *et al.*(*1*) observed that the value of $\Delta\mu("^1B_u^+")$ was dependent upon the vibronic band for which the Stark shift was measured, and ranged from 12.9 D near the absorption max to 20.8 D in the lowest energy vibronic band (*1*). The latter studies were carried out at 77 K in methyl methacrylate polymer. The Stark measurements necessarily reflect changes in dipole moments for the ground state (or Franck-Condon) geometry, and thus should be compared to the S_1 results shown in the left panel of Fig. 8. The SAC-CI calculations predict a $\Delta\mu("^1B_u^+")$ value of 15 D, which is smaller than the value reported by Premvardhan *et al.*(*2*), but is in excellent agreement with the 12.9 D value reported for the band near the Frank-Condon maximum by Kusumoto *et al.*(*1*) Some of the differences between theory and experiment can be attributed to our use of a model chromophore for the excited state calculations.

The above experimental and theoretical results are to be compared to the results predicted for the change in dipole moment of the ICT state, which is calculated to have a $\Delta\mu(\text{ICT}) = 21.1$ D relative to a ground state value of 18 D. The total dipole moment of the ICT state is calculated to be 37.7 D, which is remarkable, even for a charge transfer state. The low energy of the ICT state in polar compounds is due in large part to the interaction of this dipole moment with the reaction field of the solvent. The rapid formation of the ICT state (~100 fs, see Fig. 5 and previous discussion) is facilitated by the close alignment of the ground and S_1(ICT) states dipole moments (compare the two lower right panels in Fig. 8).

The dipole moments of the excited singlet states other than the “$1^1B_u^{+}$” and ICT states are all less than 10 D and, in the case of the second and third excited singlet state, are in roughly the opposite direction of the ground state dipole moment.

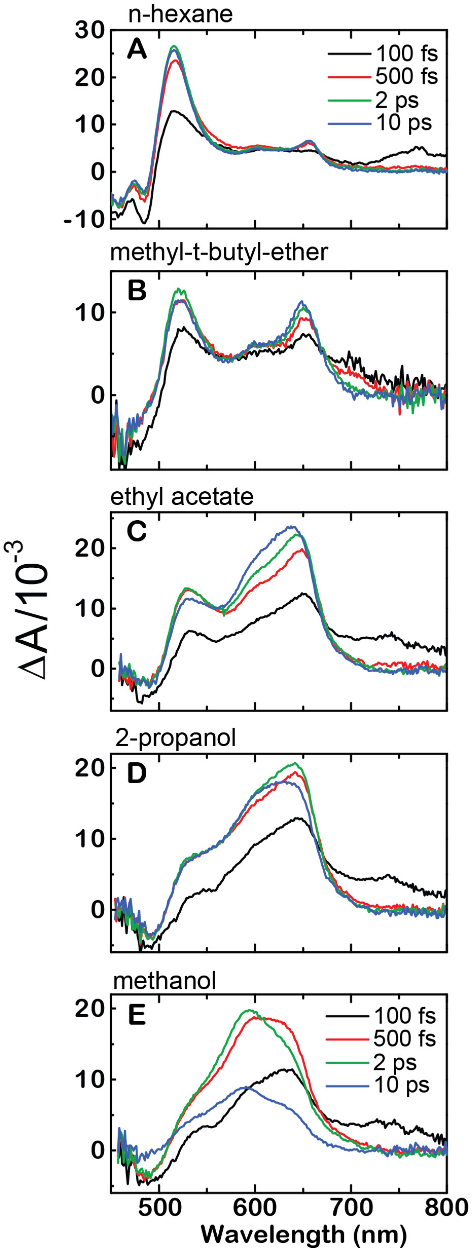
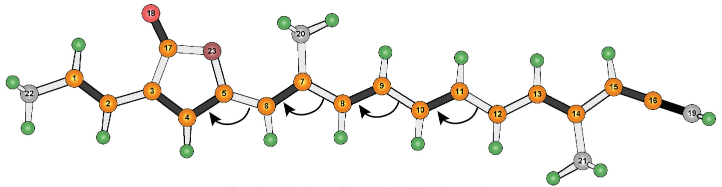
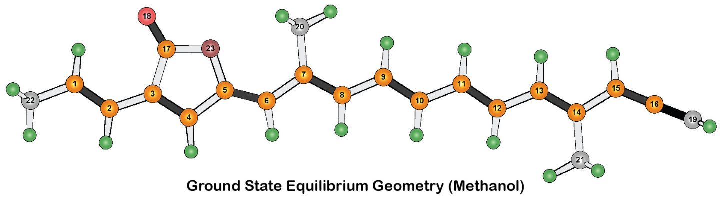


Figure S1. Transient absorption spectra of peridinin taken at different time delays upon excitation at 485 nm in *n*-hexane (A), methyl-*t*-butyl ether (B), ethyl acetate (C), 2-propanol (D), and methanol (E). The line colors reflect different time delays as shown in the two identical inserts, duplicated for reader convenience. See Figure 4 in the main paper for the shorter time delays showing the formation time of the ICT state in higher temporal resolution.



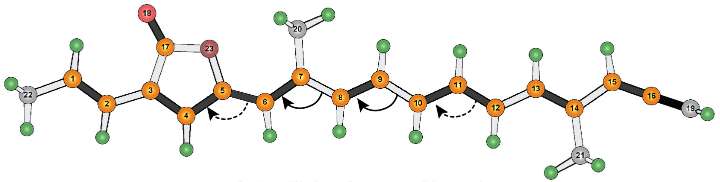
S_1 Equilibrium Geometry (Methanol)

R(1,2)= 1.3465 R(3,4)= 1.3964 R(5,6)= 1.4067 R(7,8)= 1.4460 R(9,10)= 1.4312 R(11,12)= 1.4035 R(13,14)= 1.3772 R(15,16)= 1.3217
R(2,3)= 1.4503 R(4,5)= 1.3988 R(6,7)= 1.3845 R(8,9)= 1.3671 R(10,11)= 1.3828 R(12,13)= 1.4143 R(14,15)= 1.4641
R(3,17)= 1.4479 R(17,18)= 1.2342 R(16,19)= 1.3045 R(7,20)= 1.5139 R(14,21)= 1.5078 R(1,22)= 1.5073



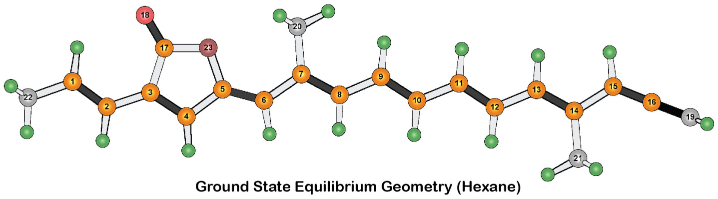
Ground State Equilibrium Geometry (Methanol)

R(1,2)= 1.3468 R(3,4)= 1.3682 R(5,6)= 1.3645 R(7,8)= 1.3784 R(9,10)= 1.3691 R(11,12)= 1.3666 R(13,14)= 1.3670 R(15,16)= 1.3213
R(2,3)= 1.4500 R(4,5)= 1.4307 R(6,7)= 1.4374 R(8,9)= 1.4277 R(10,11)= 1.4298 R(12,13)= 1.4343 R(14,15)= 1.4631
R(3,17)= 1.4762 R(17,18)= 1.2146 R(16,19)= 1.3054 R(7,20)= 1.5109 R(14,21)= 1.5067 R(1,22)= 1.4977



S_1 Equilibrium Geometry (Hexane)

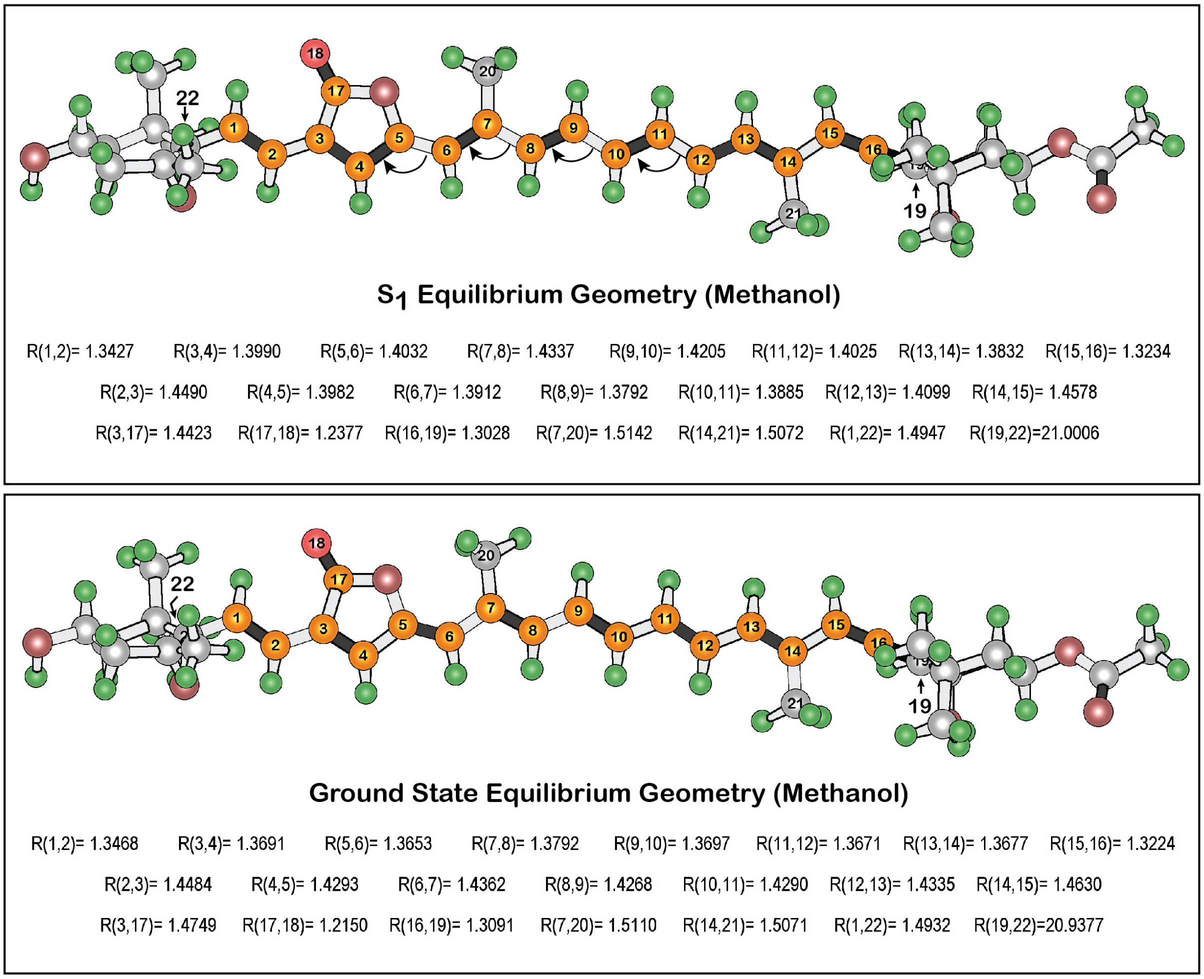
R(1,2)= 1.3473 R(3,4)= 1.3889 R(5,6)= 1.3956 R(7,8)= 1.4278 R(9,10)= 1.4132 R(11,12)= 1.3934 R(13,14)= 1.3755 R(15,16)= 1.3224
R(2,3)= 1.4473 R(4,5)= 1.4050 R(6,7)= 1.3947 R(8,9)= 1.3824 R(10,11)= 1.3948 R(12,13)= 1.4179 R(14,15)= 1.4615
R(3,17)= 1.4586 R(17,18)= 1.2241 R(16,19)= 1.3049 R(7,20)= 1.5136 R(14,21)= 1.5082 R(1,22)= 1.5058



Ground State Equilibrium Geometry (Hexane)

R(1,2)= 1.3465 R(3,4)= 1.3662 R(5,6)= 1.3638 R(7,8)= 1.3773 R(9,10)= 1.3680 R(11,12)= 1.3656 R(13,14)= 1.3662 R(15,16)= 1.3208
R(2,3)= 1.4488 R(4,5)= 1.4330 R(6,7)= 1.4384 R(8,9)= 1.4279 R(10,11)= 1.4298 R(12,13)= 1.4341 R(14,15)= 1.4626
R(3,17)= 1.4807 R(17,18)= 1.2100 R(16,19)= 1.3052 R(7,20)= 1.5107 R(14,21)= 1.5067 R(1,22)= 1.4973

Figure S2. Geometries calculated for the ground and lowest excited relaxed singlet states of the peridinin model compound in *n*-hexane and methanol. The ground state geometries were calculated using B3LYP/6-31G(d) density functional methods. The relaxed excited singlet geometry was calculated using single-configuration interaction (CIS) methods and an active space of the highest energy 8 filled and lowest energy 8 virtual molecular orbitals. The coordinates and Mulliken atomic charges for the two structures in methanol are presented in Tables S1 (ground) and S2 (S_1 relaxed geometry).



S_1 Equilibrium Geometry (Methanol)

R(1,2)= 1.3427 R(3,4)= 1.3990 R(5,6)= 1.4032 R(7,8)= 1.4337 R(9,10)= 1.4205 R(11,12)= 1.4025 R(13,14)= 1.3832 R(15,16)= 1.3234

R(2,3)= 1.4490 R(4,5)= 1.3982 R(6,7)= 1.3912 R(8,9)= 1.3792 R(10,11)= 1.3885 R(12,13)= 1.4099 R(14,15)= 1.4578

R(3,17)= 1.4423 R(17,18)= 1.2377 R(16,19)= 1.3028 R(7,20)= 1.5142 R(14,21)= 1.5072 R(1,22)= 1.4947 R(19,22)=21.0006

Ground State Equilibrium Geometry (Methanol)

R(1,2)= 1.3468 R(3,4)= 1.3691 R(5,6)= 1.3653 R(7,8)= 1.3792 R(9,10)= 1.3697 R(11,12)= 1.3671 R(13,14)= 1.3677 R(15,16)= 1.3224

R(2,3)= 1.4484 R(4,5)= 1.4293 R(6,7)= 1.4362 R(8,9)= 1.4268 R(10,11)= 1.4290 R(12,13)= 1.4335 R(14,15)= 1.4630

R(3,17)= 1.4749 R(17,18)= 1.2150 R(16,19)= 1.3091 R(7,20)= 1.5110 R(14,21)= 1.5071 R(1,22)= 1.4932 R(19,22)=20.9377

Figure S3. Geometries calculated for the ground and lowest excited relaxed singlet states of peridinin in methanol. The ground state geometries were calculated using B3LYP/6-31G(d) density functional methods. The relaxed excited singlet geometry was calculated using single-configuration interaction (Hartree-Fock CIS) methods and an active space of the highest energy 8 filled and lowest energy 8 virtual molecular orbitals. The coordinates and Mulliken atomic charges for the above structures are presented in Tables S3 (ground) and S4 (S_1 relaxed geometry).

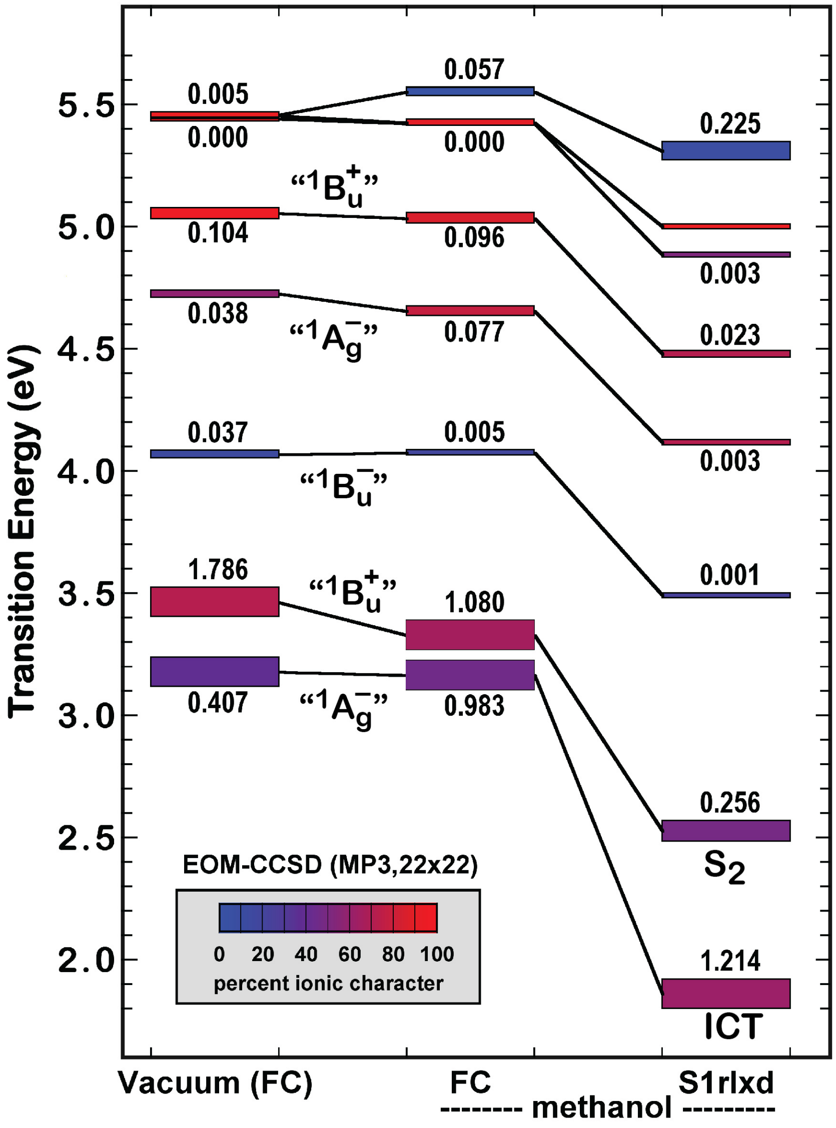


Figure S4. Effect of solvent environment on the lowest excited Franck-Condon (FC) and relaxed (S1 rlxd) singlet states of the full peridinin chromophore (Fig. S2) in methanol based on EOM-CCSD procedures. The results for a vacuum calculation (no solvent) are shown in the left column. Transition energies are relative to the ground state. These calculations were carried out with a reduced active space compared to the vacuum result for the EOM-CCSD calculation of Fig. 4 (main paper), and thus the transition energies and oscillator strengths differ slightly. The reduced active space was used to permit the use of PCM solvation for the methanol calculations.

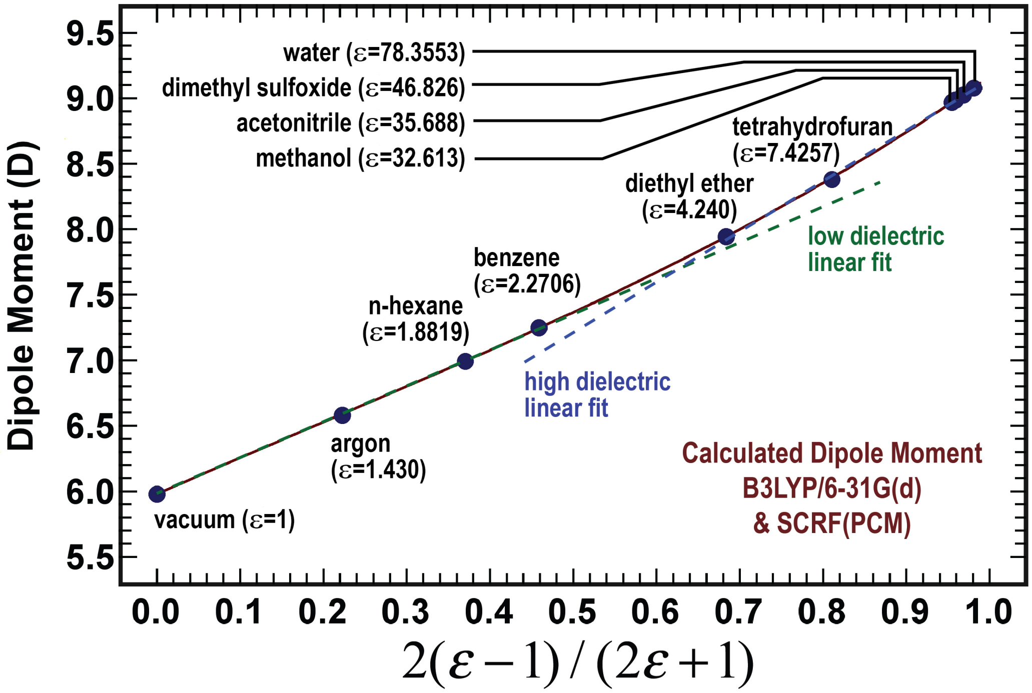


Figure S5. Ground state dipole moments of peridinin as a function of Onsager dielectric function, which spans from 0 (vacuum) to 1 (infinite dielectric constant). The results were calculated by using B3LYP/6-31G(d) density functional theory coupled with self-consistent reaction field methods based on PCM methods (see theoretical).

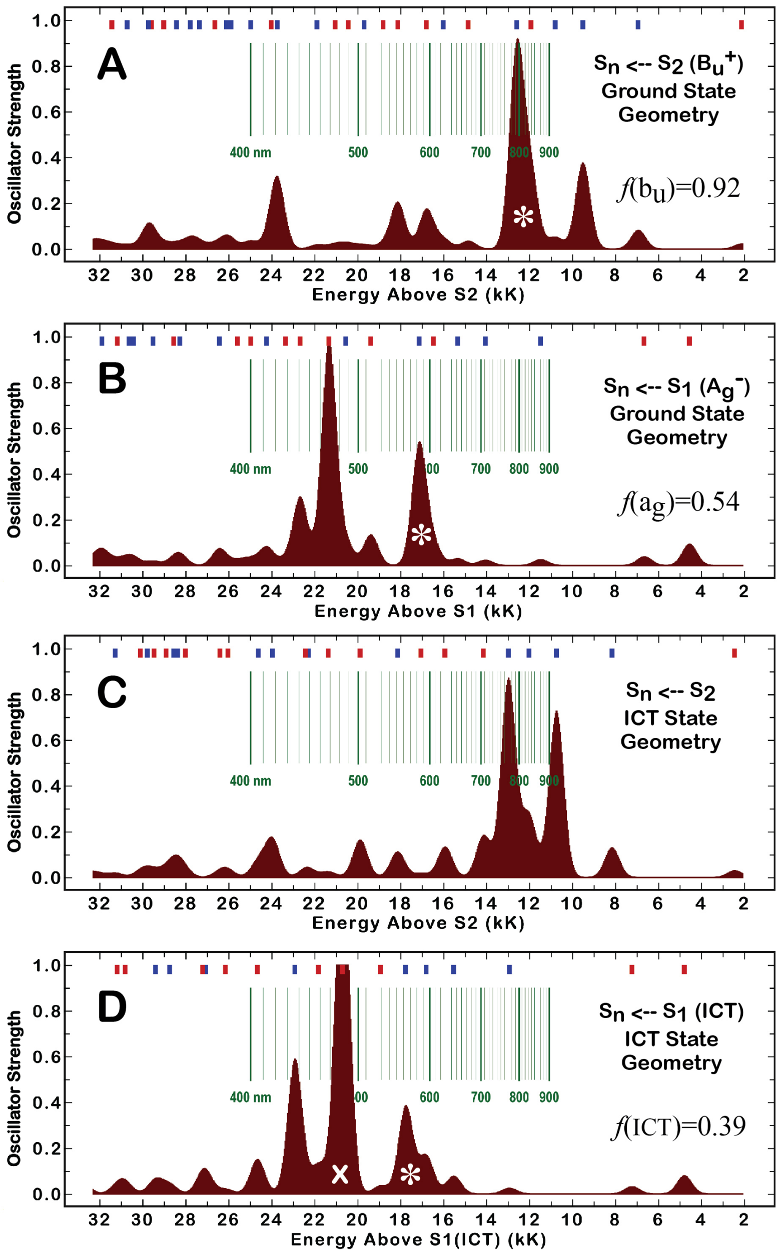


Figure S6. MNDO-PSDCI analysis of the $S_1 \rightarrow S_n$ and $S_2 \rightarrow S_n$ transient absorption spectra in vacuum. The data are plotted using an artificially narrow Gaussian bands of width 300 cm-1 the height of which is equal to the oscillator strength of the transition. Calculations A and B were carried out using the ground state geometry and calculations C and D were carried out using the ICT excited state geometry.

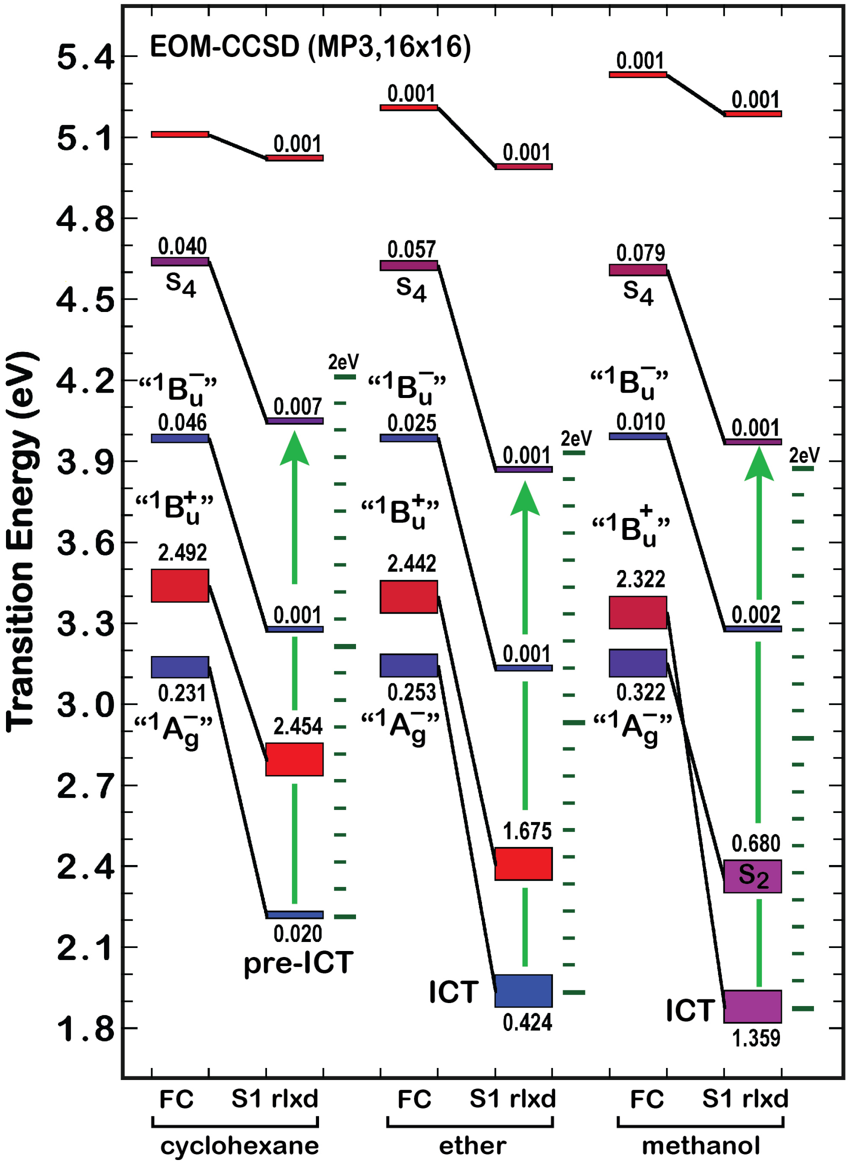


Figure S7. Analysis of the S_1(relaxed) → S_n transient absorption absorption maximum as a function of solvent environment based on EOM-CCSD calculations. This event is observed in all solvents despite the fact that the ICT state is viewed to be too polar to form in nonpolar solvents. The lowest excited singlet state does relax in all solvents, however, and has an energy and electronic properties that provide for an observable S_1(relaxed) → S_n transition. The transient absorption event assigned to the ICT state (Fig. 5, main paper) is observed to blue shift with increasing solvent polarity. The above results predict such a shift (note the green arrows, and the scale shown to the right of the relaxed excited singlet state).

Table S1. Cartesian Coordinates and Mulliken Atomic Charges of the Ground State of the Peridinin Model Compound in Methanol (see text).

Atom	X(Å)	Y(Å)	Z(Å)	Mulliken Charge
C01	-8.857381	0.346408	0.000000	-0.109052
C02	-7.757199	-0.430375	0.000000	-0.175175
C03	-6.383861	0.034867	0.000000	0.056332
C04	-5.240101	-0.716051	0.000000	-0.223483
C05	-4.102843	0.152099	0.000000	0.366756
C06	-2.781016	-0.186458	0.000000	-0.269239
C07	-1.606549	0.642302	0.000000	0.165135
C08	-0.392079	-0.009709	0.000000	-0.192538
C09	0.915465	0.563570	0.000000	-0.145188
C10	2.057080	-0.192124	0.000000	-0.131736
C11	3.382249	0.344845	0.000000	-0.140246
C12	4.513868	-0.421250	0.000000	-0.137588
C13	5.840021	0.125112	0.000000	-0.200254
C14	7.022497	-0.560857	0.000000	0.180933
C15	8.266543	0.209180	0.000000	-0.354188
C16	9.485617	-0.300317	0.000000	0.321623
C17	-5.951591	1.446345	0.000000	0.574804
O18	-6.577006	2.487563	0.000000	-0.521260
C19	10.696394	-0.788137	0.000000	-0.562002
C20	-1.733762	2.147874	0.000000	-0.523776
C21	7.138104	-2.063155	0.000000	-0.535717
C22	-10.259114	-0.180965	0.000000	-0.499447
O23	-4.559504	1.462941	0.000000	-0.532569
H24	-8.736908	1.427115	-0.050000	0.159463
H25	-7.876119	-1.514150	-0.050000	0.142798
H26	-5.170969	-1.797096	-0.050000	0.183707
H27	-2.607979	-1.260526	-0.050000	0.166567
H28	-0.420421	-1.099732	-0.050000	0.146480
H29	1.020345	1.646350	-0.050000	0.149334
H30	1.962472	-1.278935	-0.050000	0.147140
H31	3.481971	1.430937	-0.050000	0.144231
H32	4.394285	-1.503017	-0.050000	0.148661
H33	5.898842	1.214045	-0.050000	0.140114
H34	8.167521	1.295964	-0.050000	0.171066
H35	-2.290007	2.494007	0.827766	0.173277
H36	-2.290007	2.494007	-0.927766	0.173277
H37	-0.760946	2.641801	-0.050000	0.163832
H38	7.697943	-2.405728	0.829120	0.171769
H39	7.697943	-2.405728	-0.929120	0.171769
H40	6.168758	-2.563582	-0.050000	0.169099
H41	11.229153	-1.002880	-0.976312	0.183664
H42	11.229153	-1.002880	0.876312	0.183664
H43	-10.283382	-1.275782	-0.050000	0.162226
H44	-10.813739	0.176051	-0.928752	0.167870
H45	-10.813739	0.176051	0.828752	0.167870

Table S2. Cartesian Coordinates and Mulliken Atomic Charges of the Relaxed Excited Singlet State of the Peridinin Model Compound in Methanol (see text).

Atom	X(Å)	Y(Å)	Z(Å)	Mulliken Charge
C01	-8.884788	0.570023	0.000000	-0.173447
C02	-7.807427	-0.237707	0.000000	-0.300926
C03	-6.413844	0.163853	0.000000	0.102802
C04	-5.300606	-0.679191	0.000000	-0.440782
C05	-4.131238	0.088347	0.000000	0.466874
C06	-2.784098	-0.316565	0.000000	-0.459478
C07	-1.637113	0.458934	0.000000	0.417760
C08	-0.371078	-0.239603	0.000000	-0.344116
C09	0.875728	0.321105	0.000000	-0.145647
C10	2.088343	-0.439032	0.000000	-0.239116
C11	3.338862	0.151280	0.000000	-0.179607
C12	4.543751	-0.568566	0.000000	-0.180662
C13	5.809465	0.062569	0.000000	-0.316470
C14	7.038588	-0.558618	0.000000	0.386659
C15	8.228716	0.294066	0.000000	-0.317867
C16	9.475907	-0.143292	0.000000	0.052502
C17	-5.908026	1.520496	0.000000	0.401498
O18	-6.451885	2.628443	0.000000	-0.509026
C19	10.716474	-0.546762	0.000000	-0.513460
C20	-1.692345	1.971830	0.000000	-0.672219
C21	7.240949	-2.052785	0.000000	-0.694077
C22	-10.308422	0.074764	0.000000	-0.637248
O23	-4.512132	1.430126	0.000000	-0.551777
H24	-8.749940	1.635441	-0.050000	0.232222
H25	-7.966428	-1.302737	-0.050000	0.223146
H26	-5.319072	-1.746448	-0.050000	0.268526
H27	-2.660950	-1.383120	-0.050000	0.239327
H28	-0.431628	-1.313428	-0.050000	0.221472
H29	0.989347	1.388449	-0.050000	0.210487
H30	2.013591	-1.511754	-0.050000	0.227918
H31	3.397000	1.225827	-0.050000	0.221075
H32	4.482269	-1.639490	-0.050000	0.222770
H33	5.803375	1.137958	-0.050000	0.227348
H34	8.067357	1.357409	-0.050000	0.246671
H35	-2.227648	2.331410	0.818368	0.216069
H36	-2.227648	2.331410	-0.918368	0.216069
H37	-0.712140	2.417905	-0.050000	0.191657
H38	7.810767	-2.353579	0.822302	0.213851
H39	7.810767	-2.353579	-0.922302	0.213851
H40	6.314175	-2.602131	-0.050000	0.210019
H41	11.248183	-0.721380	-0.968287	0.236542
H42	11.248183	-0.721380	0.868287	0.236542
H43	-10.356432	-1.007517	-0.050000	0.186639
H44	-10.843453	0.438510	-0.922628	0.192813
H45	-10.843453	0.438510	0.822628	0.192813

Table S3. Cartesian Coordinates and Mulliken Atomic Charges of the Ground State of Peridinin in Methanol (see text).

Atom	X(Å)	Y(Å)	Z(Å)	Mulliken Charge
C01	-10.067420	0.717369	0.030370	-0.199398
C02	-8.971288	-0.065150	0.041882	-0.168848
C03	-7.601222	0.396805	-0.043369	0.058653
C04	-6.457292	-0.355449	-0.038150	-0.221210
C05	-5.323455	0.509338	-0.134937	0.363811
C06	-4.000924	0.170601	-0.153659	-0.265969
C07	-2.829380	0.997453	-0.234589	0.164044
C08	-1.614173	0.345366	-0.219614	-0.190565
C09	-0.307524	0.915978	-0.271890	-0.145916
C10	0.833195	0.158491	-0.240952	-0.130435
C11	2.159328	0.689934	-0.274264	-0.141191
C12	3.287429	-0.081104	-0.231455	-0.135966
C13	4.616709	0.455171	-0.245856	-0.198064
C14	5.793000	-0.240485	-0.191496	0.180689
C15	7.044876	0.516640	-0.189566	-0.407804
C16	8.257173	-0.009336	-0.141617	0.242399
C17	-7.171942	1.803668	-0.152537	0.580092
O18	-7.800147	2.842679	-0.198893	-0.523088
C19	9.462676	-0.517180	-0.090222	-0.065413
C20	-2.958041	2.500265	-0.324301	-0.523598
C21	5.890315	-1.742443	-0.114222	-0.540786
C22	-11.462199	0.188909	0.101698	0.265280
O23	-5.781465	1.818445	-0.203643	-0.533184
C24	-12.045844	-0.222519	1.422133	0.287573
O25	-11.570947	-1.203489	0.460849	-0.537050
C26	-11.243086	-0.149770	2.704260	-0.496893
C27	-13.557523	-0.257777	1.640985	-0.315986
C28	-14.391088	0.378613	0.522696	0.129645
C29	-13.812650	0.050664	-0.851347	-0.298688
C30	-12.387755	0.616913	-1.066828	0.058452
C31	-11.829323	0.037927	-2.382716	-0.462296
O32	-15.769228	0.004815	0.631393	-0.665630
C33	10.211791	-0.857374	-1.397264	0.265044
C34	9.529529	-0.285374	-2.644837	-0.471354
O35	10.208039	-2.300720	-1.479672	-0.657006
C36	11.666402	-0.344404	-1.317591	-0.306045
C37	12.367805	-0.820327	-0.054080	0.126479
C38	11.634180	-0.337732	1.192960	-0.289191
C39	10.157371	-0.808738	1.264172	0.054876
C40	9.474367	-0.043373	2.412608	-0.460575
O41	13.708543	-0.249359	-0.085140	-0.478883
C42	-12.440048	2.158613	-1.172598	-0.475948
C43	14.692762	-0.921895	0.547426	0.614909
C44	16.008876	-0.193215	0.419608	-0.529738
O45	14.528740	-1.972240	1.138714	-0.511813
C46	10.084774	-2.321991	1.585281	-0.456752
H47	10.099125	-0.571736	-3.587253	0.148346
H48	-13.803474	0.218547	2.546330	0.156312
H49	-13.841326	-1.316037	1.686835	0.151946
H50	-14.403640	1.465036	0.609831	0.145095

Table S3 (continued)

Atom	X(Å)	Y(Å)	Z(Å)	Mulliken Charge
H51	-14.475784	0.455161	-1.675405	0.142756
H52	-13.794013	-1.039976	-1.026878	0.140535
H53	-9.955009	1.793194	-0.106942	0.172461
H54	-9.103037	-1.141928	0.076913	0.154556
H55	-6.387751	-1.434198	-0.019798	0.185846
H56	-3.826811	-0.901507	-0.141225	0.168070
H57	-1.642799	-0.742694	-0.204468	0.147614
H58	-0.201502	1.996897	-0.382567	0.149608
H59	0.735675	-0.926462	-0.231225	0.148028
H60	2.263850	1.774120	-0.379500	0.144309
H61	3.161228	-1.160637	-0.224402	0.148955
H62	4.685342	1.542378	-0.345923	0.139328
H63	6.952620	1.603916	-0.276869	0.167544
H64	12.161616	-0.682554	2.039924	0.152985
H65	11.663744	0.760183	1.148499	0.146196
H66	12.468787	-1.906485	-0.104646	0.163521
H67	12.215425	-0.683633	-2.255580	0.151496
H68	11.665210	0.752676	-1.387834	0.156127
H69	15.937083	0.790953	0.844409	0.194731
H70	16.251037	-0.031482	-0.685426	0.192645
H71	16.798733	-0.773790	0.847265	0.181815
H72	-11.458779	0.785131	3.184277	0.161407
H73	-10.169945	-0.204894	2.465994	0.163533
H74	-11.525891	-0.979079	3.314201	0.160023
H75	-11.479665	2.572715	-1.545132	0.156380
H76	-12.705364	2.634731	-0.272195	0.156018
H77	-13.188724	2.454398	-1.966370	0.153964
H78	-11.742443	-1.052711	-2.372449	0.151364
H79	-10.839642	0.446388	-2.663129	0.149495
H80	-12.498204	0.279678	-3.267136	0.148484
H81	-3.492383	2.900420	0.494014	0.173458
H82	-3.536658	2.791618	-1.257490	0.173474
H83	-1.986092	2.992848	-0.429867	0.163962
H84	6.293689	-2.052354	0.808659	0.176413
H85	6.584549	-2.121888	-0.923192	0.171994
H86	4.928613	-2.238546	-0.304107	0.168565
H87	8.435866	-0.364321	2.493130	0.150887
H88	9.475577	1.036938	2.180535	0.147162
H89	10.006627	-0.232207	3.302124	0.146570
H90	10.545226	-2.932540	0.757120	0.170767
H91	9.039354	-2.636608	1.631450	0.146450
H92	10.588870	-2.523498	2.488678	0.142471
H93	9.479425	0.807389	-2.661884	0.156331
H94	8.514541	-0.679157	-2.793733	0.161309
H95	-15.818440	-0.954868	0.434846	0.402905
H96	10.701651	-2.542738	-2.332136	0.409126

Table S4. Cartesian Coordinates and Mulliken Atomic Charges of the Relaxed Excited Singlet State of Peridinin in Methanol (see text).

Atom	X(Å)	Y(Å)	Z(Å)	Mulliken Charge
C01	-10.118054	0.635324	0.051360	-0.329891
C02	-9.018357	-0.132706	-0.009332	-0.281481
C03	-7.642886	0.322912	-0.001083	0.076570
C04	-6.495209	-0.475377	-0.052407	-0.411696
C05	-5.356580	0.335641	-0.026877	0.416133
C06	-4.001589	-0.028298	-0.051450	-0.413546
C07	-2.843022	0.741703	-0.034169	0.352359
C08	-1.593532	0.038975	-0.056085	-0.291214
C09	-0.342817	0.620131	-0.048994	-0.198957
C10	0.862640	-0.131277	-0.062362	-0.186896
C11	2.124212	0.448587	-0.062089	-0.217928
C12	3.313575	-0.294574	-0.068373	-0.153863
C13	4.588842	0.306702	-0.074949	-0.352495
C14	5.807269	-0.347960	-0.072594	0.414478
C15	7.011855	0.473110	-0.074706	-0.372747
C16	8.248910	0.002923	-0.077982	-0.053555
C17	-7.194702	1.692476	0.058467	0.409435
O18	-7.789834	2.776090	0.116971	-0.531566
C19	9.481761	-0.418177	-0.079525	0.340171
C20	-2.834761	2.255360	0.006003	-0.739602
C21	5.964118	-1.846824	-0.048508	-0.700066
C22	-11.512243	0.097187	0.024835	0.314514
O23	-5.799918	1.665559	0.040151	-0.558155
C24	-12.143612	-0.427311	1.279092	0.386352
O25	-11.617946	-1.358564	0.245400	-0.580197
C26	-11.394259	-0.470161	2.591538	-0.687538
C27	-13.657412	-0.496957	1.442566	-0.454200
C28	-14.452963	0.218434	0.347775	0.089764
C29	-13.825286	0.016413	-1.027864	-0.444248
C30	-12.400378	0.614767	-1.129683	0.203450
C31	-11.795681	0.175230	-2.480724	-0.657123
O32	-15.834727	-0.220845	0.365820	-0.702286
C33	10.210211	-0.653416	-1.417671	0.229114
C34	9.447467	-0.116442	-2.634016	-0.638297
O35	10.328807	-2.101724	-1.538026	-0.710357
C36	11.622125	-0.037735	-1.368505	-0.465299
C37	12.389596	-0.495811	-0.138929	0.183075
C38	11.668423	-0.100875	1.145883	-0.418667
C39	10.237743	-0.693511	1.247017	0.095539
C40	9.533171	-0.015243	2.441039	-0.628776
O41	13.682906	0.200340	-0.195077	-0.559947
C42	-12.469154	2.162155	-1.084233	-0.665964
C43	14.800041	-0.321098	0.343673	0.619630
C44	15.990553	0.572951	0.162240	-0.664415
O45	14.814150	-1.407770	0.911982	-0.497826
C46	10.295119	-2.217507	1.529658	-0.619304
H47	10.013717	-0.318985	-3.586267	0.196749
H48	-13.930120	-0.088980	2.356613	0.203458
H49	-13.929310	-1.547704	1.404843	0.191658
H50	-14.523345	1.269752	0.521797	0.217404

Table S4 (continued)

H51	-14.452372	0.484263	-1.827450	0.206896
H52	-13.789364	-1.044255	-1.301494	0.186385
H53	-10.027494	1.700946	0.061125	0.267653
H54	-9.146991	-1.198531	-0.114760	0.248285
H55	-6.473047	-1.542002	-0.152384	0.266690
H56	-3.866650	-1.094175	-0.139218	0.228949
H57	-1.642810	-1.035479	-0.128077	0.223959
H58	-0.251616	1.689892	-0.081632	0.229270
H59	0.787696	-1.204646	-0.122282	0.225687
H60	2.196287	1.521620	-0.106408	0.227372
H61	3.228972	-1.364379	-0.116800	0.221717
H62	4.610573	1.381420	-0.130384	0.230645
H63	6.872029	1.539438	-0.122249	0.249609
H64	12.238059	-0.422584	1.958715	0.219052
H65	11.610798	0.981787	1.128066	0.195254
H66	12.584431	-1.554258	-0.224999	0.243574
H67	12.160839	-0.313724	-2.316803	0.227304
H68	11.541224	1.041948	-1.404453	0.200702
H69	15.805802	1.522145	0.596857	0.227769
H70	16.145374	0.762405	-0.941010	0.227521
H71	16.868845	0.113147	0.534703	0.217338
H72	-11.581357	0.436562	3.105708	0.193782
H73	-10.330949	-0.571380	2.395711	0.218988
H74	-11.743483	-1.310907	3.131346	0.194851
H75	-11.520805	2.605670	-1.408572	0.198337
H76	-12.737632	2.536125	-0.152899	0.189504
H77	-13.210974	2.516089	-1.841044	0.197179
H78	-11.697252	-0.903164	-2.577128	0.194010
H79	-10.818450	0.613295	-2.689891	0.197658
H80	-12.441492	0.491452	-3.343439	0.188602
H81	-2.317048	2.609279	0.841819	0.200726
H82	-3.830039	2.659354	-0.037561	0.264043
H83	-2.309587	2.654871	-0.905563	0.200226
H84	6.371518	-2.159191	0.857482	0.217388
H85	6.662645	-2.165868	-0.861765	0.217241
H86	5.034928	-2.369610	-0.252971	0.211526
H87	8.545027	-0.427927	2.553945	0.193640
H88	9.434926	1.053371	2.239514	0.188071
H89	10.112964	-0.177022	3.292743	0.192268
H90	10.797272	-2.762945	0.697199	0.221252
H91	9.292238	-2.618141	1.573032	0.184125
H92	10.815795	-2.389568	2.416047	0.182665
H93	9.299467	0.952756	-2.613900	0.196772
H94	8.482513	-0.595428	-2.776196	0.207232
H95	-15.935122	-1.145345	0.098815	0.402119
H96	10.704805	-2.374194	-2.423739	0.424413

Supporting References

1. Kusumoto, T., T. Horibe, T. Kajikawa, S. Hasegawa, T. Iwashita, R. J. Cogdell, R. R. Birge, H. A. Frank, S. Katsumura, and H. Hashimoto. 2010. Stark absorption spectroscopy of peridinin and allene-modified analogues. Chem. Phys. 373:71-79.
2. Premvardhan, L., E. Papagiannakis, R. G. Hiller, and R. van Grondelle. 2005. The charge-transfer character of the $S_0 \rightarrow S_2$ transition in the carotenoid peridinin is revealed by Stark sprectroscopy. J. Phys. Chem. B. 109:15589-15597.